

Jiri Konicek

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CARBOXYLIC ACIDS, AMINES AND N- SUBSTITUTED AMIDES

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by

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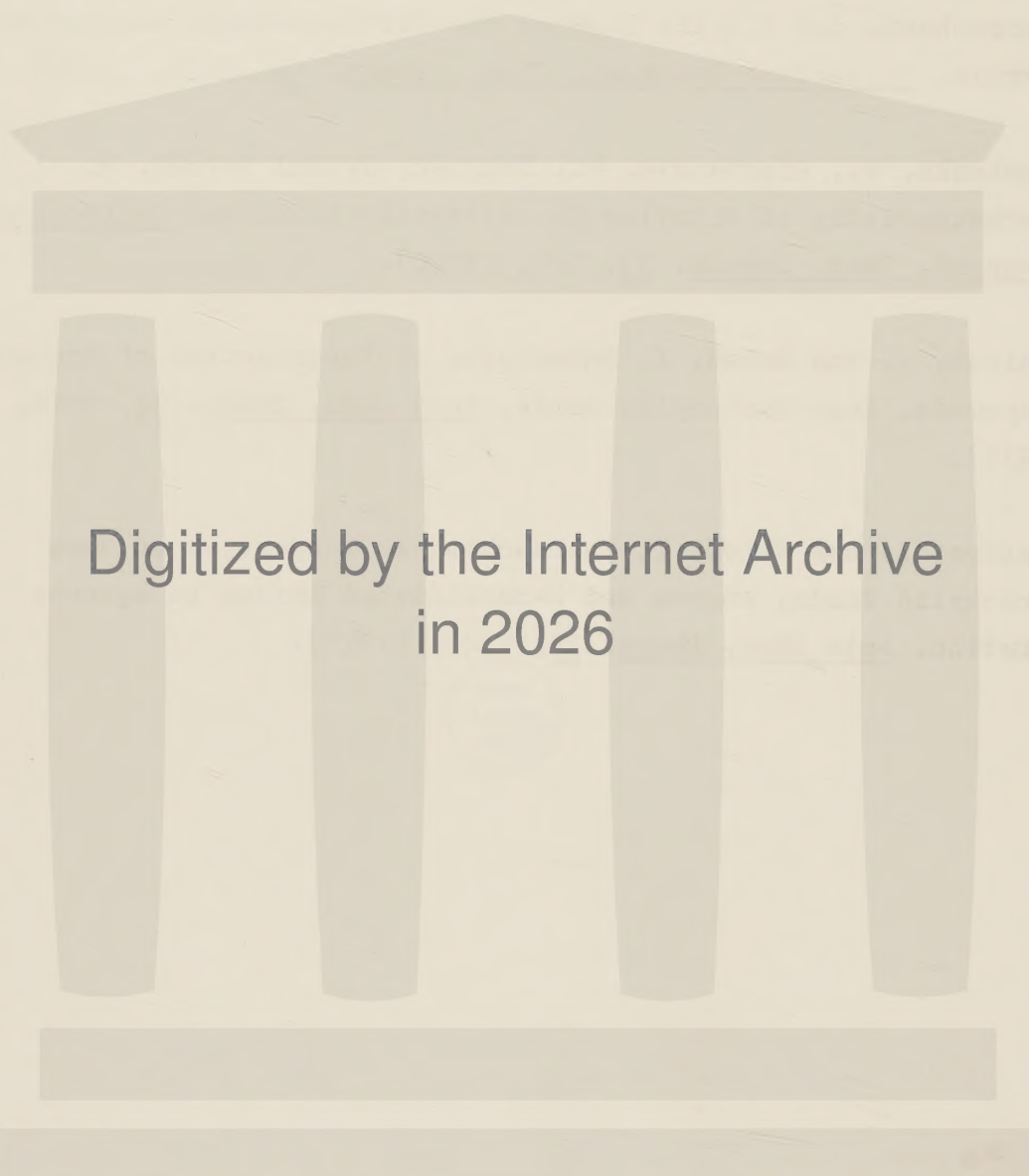
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This review gives a summary of the results from the following papers which will be referred to by the Roman numerals I-V.

- I. Konicek, J. Design and Testing of a Vaporisation Calorimeter. Enthalpies of Vaporisation of Some Alkyl Cyanides. Acta Chem. Scand. 26, (1973). In press.
- II. Konicek, J., Prochazka, M., Krestanova, V. and Smisek, M. Thermochemie der Nitrile I. Über die Bildungswärmen aliphatischer Nitrile. Collection Czechosl. Chem. Commun. 34, 2249, (1969)
- III. Prochazka, M., Krestanova, V., Konicek, J. and Smisek, M. Thermochemistry of Nitriles II. Alicyclic Nitriles. Collection Czechosl. Chem. Commun. 35, 727, (1970).
- IV. Konicek, J. and Wadsö, I. Enthalpies of Vaporisation of Organic Compounds. Some Carboxylic Acids. Acta Chem. Scand. 24, 2612, (1970).
- V. Konicek, J. and Wadsö, I. Thermochemical Properties of Some Carboxylic Acids, Amines and N-Substituted Amides in Aqueous Solution. Acta Chem. Scand. 25, 1541, (1971).



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INTRODUCTION

A calorimeter for measurement of vaporisation enthalpies of small liquid samples was designed and tested (Paper I). The calorimeter was used for measurement on a series of alkylcyanides at 25°C.

Enthalpies of combustion of some alkylcyanides were measured (Paper II, III). Their enthalpies of formation in the ideal gas state at 25°C were derived. The contribution of the -CN group to the enthalpy of formation was determined and conjugation and cis-trans isomerisation effects were discussed.

Vaporisation enthalpies are often auxiliary data in thermochemistry and are used to establish the enthalpy values in the ideal gas state. Often, direct experimental vaporisation enthalpies can be used, provided the behaviour of studied compounds in the gas phase is ideal. Deviations from the ideal gas state have to be accounted for. Carboxylic acids are associated in the gas phase at saturation pressure and room temperature. Enthalpies of vaporisation of some lower carboxylic acids, were measured calorimetrically and corrections were made for the ideal gas state (Paper IV).

The behaviour of some carboxylic acids, amines and amides in water was investigated by means of solution calorimetry (Paper V). An attempt has been made to correlate properties such as enthalpy of solution, enthalpy of solvation and heat capacities of solution to the molecular structure.

CALORIMETRIC METHODS USED IN THIS WORK

A combustion calorimeter

A calorimeter was designed for the measurement of enthalpies of combustion (1). The calorimeter was of an aneroid type with a massive copper bomb. The inside walls of the bomb were platinum-lined. The temperature of the bomb was measured by means of a platinum resistance thermometer which formed a part of a Wheatstone bridge. The bridge was supplied by alternating current.

The bomb was surrounded by a copper jacket, the temperature of which was controlled within $\pm 5 \cdot 10^{-4}$ °C by means of an electronic proportional regulator. An outer thermostated jacket made of duraluminium was controlled within $\pm 5 \cdot 10^{-2}$ °C. The calorimeter was designed for measurement of heat quantities of about 2 kJ.

Benzoic acid was used as a standard substance to determine the "water equivalent" of the calorimeter with a precision of $\pm 0.01\%$. The accuracy of enthalpy of combustion measurements was usually $\pm 0.025\%$ or better for solid compounds. Liquid compounds were sealed into Mylar bags before the measurements. The accuracy of the measurements for liquid substances was $\pm 0.04\%$ or better.

A vaporisation calorimeter (Paper I)

A calorimeter was designed for the measurement of enthalpies of vaporisation and was used in the study described in Paper II, III. The calorimeter consists of a vaporisation vessel connected by a glass tube to a condensation bulb. The vaporisation vessel fits accurately into a copper cylinder with a resistance thermometer and a calibrated heater on its surface. The temperature of a surrounding jacket is kept constant during the experiment within $\pm 5 \cdot 10^{-4}^{\circ}\text{C}$. Only the substance which is being investigated is present (as liquid and vapour) in the vaporisation system. Before an experiment the liquid sample is condensed in the vaporisation vessel at chosen temperature (25°C) while the temperature of the tube and bulb is kept somewhat higher ($25,3^{\circ}\text{C}$). By cooling the condensation bulb, the substance can be evaporated from the calorimeter. The temperature of the calorimeter is maintained constant by means of an electronically controlled, calibrated, heater. The energy supplied to the calorimeter is calculated from the measured heating time and the heat effect. The energy measured corresponds to the enthalpy of vaporisation of the sample, provided the vaporisation process is carried out close to the equilibrium condition. An excessive cooling of the condensation bulb can result in a pressure drop within the system and an error can be introduced by an incomplete PV-work. The wrong values of enthalpy of vaporisation obtained on a similar type of calorimeter (2) were, as noted by Morawetz (3), probably caused by this type of error. It is believed that this error was avoided in the present design due to the good heat conductivity of the metallic vaporisation vessel used.

The use of the massive metallic vaporisation vessel made possible the complete vaporisation of the liquid sample present in the calorimeter. The minimum amount of a substance necessary for the measurement was thus considerably reduced as compared to the other instruments of similar type (2, 4). For samples consuming an energy of totally about 200 J enthalpies of vaporisation can be measured with an accuracy of $\pm 0.25\%$. A somewhat higher accuracy can be achieved for larger samples. For the measurement

of enthalpies of vaporisation of carboxylic acids (Paper IV) a different vaporisation calorimeter was used (5).

Enthalpy of solution and heat capacity calorimeters

Enthalpies of solution were measured on a LKB 8721-1 Precision Calorimeter, using a 100 ml reaction vessel. The measurements were performed at 20, 25 and 30°C.

A new drop calorimeter for heat capacity measurement was used (6). A twin microcalorimetric unit, kept at 28°C was used as the receiver of the sample, which was thermostated to 22°C before the experiment. Heat capacity values at 25°C were established with an accuracy of $\pm 0.5\%$.

ENTHALPIES OF FORMATION OF SOME CYANIDES (PAPER II, III)

A shift towards conjugated isomers has been observed by Vilim in equilibrium studies on non-saturated cyanides (7). The position of the equilibria suggest that a stabilisation of conjugated cyanides takes place. Furthermore, unlike hydrocarbons, cis isomers of non-saturated and conjugated cyanides have been found to be more stable than trans isomers.

Cyanides form one group of compounds for which relatively few thermochemical data are available. Some of the old data on enthalpy of combustion (8, 9) are, as noted by Evans et al. (10) in error by about ± 10 kJ/mol. There are but few modern data on enthalpy of formation of cyanides available (11, 12). A thermochemical investigation on a series of cyanides has been made (II, III) in order to establish the values of the stabilising effects. Enthalpies of formation in gaseous state were derived from experimental enthalpies of combustion and vaporisation measured at 25°C. The formation enthalpy values have been used to derive the basic group contribution value of the -CN group in a simple bond energy scheme proposed by Franklin (13).

Bond energy schemes have been proposed more recently (14, 15) which lead to more accurate results for many classes of compounds. A larger number of experimental parameters is, however, needed to calculate the necessary terms for non-bonding interactions. The advantage over more simple schemes appears mainly for highly branched compounds. From the presented results only the contribution of the cyanide group attached to a primary carbon atom could have been derived.

Enthalpies of formation in gaseous state of cyanides and of corresponding hydrocarbons, in which the -CN group was substituted by a -CH₃ group, were

used to evaluate the stabilisation effects. The results are summarised in Table 1. $\Delta H_f^\circ (g)$ and $\Delta H_f^\circ (g, hc)$ are the enthalpies of formation of the cyanides and the hydrocarbons respectively. The difference between these two values, $\Delta(\Delta H_f^\circ)$, is defined by equation:

$$\Delta(\Delta H_f^\circ) = \Delta H_f^\circ (g) - \Delta H_f^\circ (g, hc) \quad (1)$$

The values of $\Delta(\Delta H_f^\circ)$ for linear saturated cyanides are $157,3 \pm 0,5$ kJ/mol for propyl-CN (10) and $157,5 \pm 1,6$ kJ/mol for butyl-CN. It can be seen on the values for allyl-CN and trans-2-butenyl-CN that the contribution of a -CN group in primary position is essentially constant and has a value of $K = 157,5$ kJ/mol. Franklin's scheme is based on a substitution of a hydrogen atom by a functional group. The value in his study based on the old and probably inaccurate data (16) was 123,4 kJ/mol. On the basis of the presented results (II) and (10) a contribution of about 115 kJ/mol was obtained.

Bond energy schemes can be used to derive values for stabilising or destabilising effects as differences between experimental and calculated enthalpies of formation. In the case of cyanides the value of the resonance of the -CN group with the conjugated double bond was established using the corresponding hydrocarbons as reference compounds. A stabilisation energy E , relative to hydrocarbons, can be expressed by equation:

$$E = K - \Delta(\Delta H_f^\circ) = 157,5 - \Delta(\Delta H_f^\circ) \text{ kJ/mol} \quad (2)$$

The average value of E is 5,85 kJ/mol for trans conjugated cyanides and 15,95 kJ/mol for cis conjugated cyanides. The value of about 5,85 kJ/mol derived from trans conjugated cyanides can be considered as the conjugation energy, relative to the hydrocarbons.

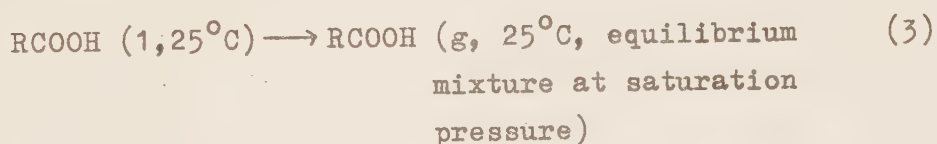
The high value of the stabilising effect for cis cyanides is not entirely caused by the conjugation. A similar higher stability of cis-isomers as compared to trans-isomers was noted for 1,2-dichloroethylene (17), and 1-bromopropylene (18) and others (19). Pitzer (20) explains the higher stability of cis-1,2-dichloroethylene by a delocalisation of a negative charge on one of the chlorine atoms and of a positive charge on the other one, the interaction of the opposite charges causing the abnormal stability of the cis-isomer. In the case of conjugated cyanides, a negative charge is located on the nitrogen atom (21). The stabilisation of cis-isomers can, therefore, be explained similarly as for cis-1,2-dichloroethylene. The interaction between the opposite charges may be the reason for a lower dipole

moments of cis-compounds (compare 4,5 D for trans-1-propenyl cyanide, with 4,08 D for the cis-isomer).

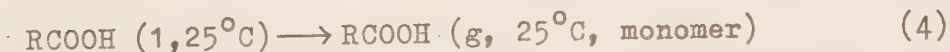
The contribution of the -CN group has been derived from linear cyanides where the group is adjacent to the primary carbon atom while in alicyclic isomers the group is attached to the secondary carbon atom. The mean value of $\Delta(\Delta H_f^0)$ is 148,6 kJ/mol for non-conjugated cyclic cyanides. From the results for linear compounds values lower by about 6 kJ/mol should have been expected for conjugated isomers. However similar values of $\Delta(\Delta H_f^0)$ were observed for 1-cyclopenten-1-yl-CN and 1-cyclohexen-1-yl-CN, which fact suggests a low value of conjugation for these compounds.

ENTHALPIES OF VAPORISATION OF SOME CARBOXYLIC ACIDS (Paper IV)

Vaporisation enthalpies of some carboxylic acids were measured calorimetrically. Lower carboxylic acids are highly associated in the vapour phase at the saturated pressure and the room temperature. Thus the experimental values refer to the process:



In order to obtain the ideal vaporisation enthalpies for the process:



appropriate corrections have to be calculated. The corrected, ideal vaporisation enthalpies, ΔH_v^0 , were calculated using the equation:

$$\Delta H_v^0 = \Delta H_v (\text{exp}) + \Delta H_{\text{diss}}^0 \cdot (1 - \alpha) \quad (5)$$

$\Delta H_v (\text{exp})$ is the experimental vaporisation enthalpy, ΔH_{diss}^0 is the dissociation enthalpy and α is the degree of dissociation.

For the dissociation enthalpy the value of 29 ± 2 kJ/mol was used (22) for all the acids studied. The degree of dissociation was calculated from gas phase equilibrium data between monomer and associated molecules, for formic acid (23), for acetic acid (24), for propionic acid (25, 26) and for butyric and isobutyric acids (25). Most of the equilibrium data were derived from the investigations at higher temperatures. In the present study, they were extrapolated to the room temperature. The estimated accuracy of the derived ΔH_v^0 values is not particularly high except for the formic acid. Partly, the uncertainty is introduced by the uncertain

$\Delta H_{\text{diss}}^{\circ}$ value but mainly by the uncertainty introduced from the equilibrium data on the degree of dissociation α .

The experimental and calculated vaporisation enthalpies are summarised in Table 2. The $\Delta H_{\text{v}}^{\circ}$ values of the carboxylic acids were used in Paper V to derive solvation enthalpies for these compounds.

THERMOCHEMICAL PROPERTIES OF SOME PROTEIN CONSTITUENTS IN WATER SOLUTION (Paper V)

The complex and not yet understood structure of water has been the object of careful studies by most physico-chemical methods available. Different models have been suggested (e.g. 27, 28), trying to account for its peculiar properties, e.g. negative volume change connected with the melting of ice, the density maximum of liquid water at 3,98°C, high dielectric constant, viscosity, thermal conductivity and high heat capacity.

Solutions of non-electrolyte solutes in water show abnormalities such as negative relative partial molar volumes, positive apparent heat capacities, viscosity - composition maxima etc. The Frank - Wen's model (28) of liquid water, which suggests the existence of a dynamic equilibrium of highly ordered, short-lived hydrogen bonded clusters with dense non-hydrogen bonded water molecules has indeed been successful in an, at least qualitative, account for some of these properties.

The structure, behaviour and reactions of proteins in water solutions are of greatest importance in protein chemistry. Proteins themselves are very complex molecules and it has been long felt and recognised that a considerable amount of information may be advantageously obtained by studying the thermodynamics of simpler compounds in water solutions. For instance amino acids (29) and peptides, carboxylic acids, amino acids (30), tetrabutylammonium salts of carboxylic acid (31), have been chosen for this purpose. Nevertheless these compounds are rather complex due to their ionic character and, consequently, effects such as dissociation were sometimes not accounted for (30).

Series of amides, amines and carboxylic acids has been chosen as suitable model compounds (V) and their aqueous heats of solution were measured. Enthalpies of solution of amides were measured in pure water, those of carboxylic acids and amines were measured in 0,1 N hydrochloric acid and 0,1 N NaOH, respectively, for suppressing the ionisation of these compounds. Different concentrations were used, ranging usually from about 0,02 mol/l to

about 0,2 mol/l. By linear extrapolation, the values at infinite dilution, $\Delta H_{\text{soln}}^{\circ}$, were obtained. For compounds for which enthalpies of vaporisation were available, the enthalpies of solvation, $\Delta H_{\text{solv}}^{\circ}$, were derived. Heat capacities, C_p° , were measured for all pure compounds investigated. Heat capacity of the solution process, ΔC_{p2}° , and partial molar heat capacities at infinite dilution, $\bar{C}_{p2}^{\circ}$, were derived. The results are summarised in Table 3.

Attempts have been made to find regularities and to correlate enthalpies of solution of organic solutes with the molecular structure. For different solutes, having a straight alkyl chain attached to a polar functional group, Corkhill (32) suggested a rule, stating that a minimum $\Delta H_{\text{soln}}^{\circ}$ in a homologue series is reached for compounds with carbon number between 3 and 5. In Fig. 1 the values of $\Delta H_{\text{soln}}^{\circ}$ of some straight chain carboxylic acids, amines, alcohols and N-substituted amides are plotted against alkyl carbon numbers (the $-\text{COOH}$ and $-\text{CONH}-$ groups are considered as function groups and their carbon atom is not included in the carbon number). Aveyard et al. (33), suggest on the basis of their experimental data, a linear dependence of $\Delta H_{\text{soln}}^{\circ}$ on the carbon number for alcohols from ethanol to C_{10} , with an increment of about 1,26 kJ/mol per $-\text{CH}_2-$ group. Their experimental values are about 1-1,5 kJ/mol lower than those of Alexander and Hill (34) or Arnett et al. (35), which indicate $-\text{CH}_2-$ increments of 0,03; 0,85 and 1,47 kJ/mol respectively, for aliphatic alcohols C_2-C_5 .

The values in (33) are probably not accurate and, at least, ethanol does not fit into the linearity concept. Measurements by Kinoshita et al. (36) indicate the values of $\Delta G_{\text{soln}}^{\circ}$ of higher aliphatic alcohols (C_4-C_{10}) which are linearly dependent on the carbon number. This would support the assumption of a linearity of $\Delta H_{\text{soln}}^{\circ}$ for higher alcohols, assuming that non-linear entropy and enthalpy of solution do not exactly compensate for each other. Among others the enthalpies of solution of non-branched amines were measured for C_3-C_6 (V) and a linear dependence of $\Delta H_{\text{soln}}^{\circ}$ on carbon number was observed, the $-\text{CH}_2-$ increment being approximately 1,32 kJ/mol. The $\Delta H_{\text{soln}}^{\circ}$ values for lower amines fit approximately on the extrapolated plot of other amines and do not follow the rule, suggested by Corkhill (32), but are judged to be uncertain. This $-\text{CH}_2-$ increment observed for amines is not very far from that suggested for alcohols (33), indicating that their assumption may be true, but their experimental data are probably biased with a systematic error.

Some similarity may be observed between the curves for alcohols and

carboxylic acids for C_2-C_4 . Also, the CH_2 -increment for amines, alcohols and amides C_4-C_5 is between 1-1,5 kJ/mol, and the plots are approximately parallel. The deviation from parallelity is, however, very large for compounds with carbon number 1 for n-alkyl compounds and 2 and 3 for n-di-alkyl compounds. There is little doubt that the functional group influences the nearest $-CH_2$ -group most, the next nearest less and the further ones probably very little. In case of di-n-alkyl amides, the plot becomes approximately parallel with those of other compounds at C_4-C_6 . The similarity of the plots seems to indicate that the $\Delta H_{\text{soln}}^{\circ}$ of ethyl- NH_2 should be about -24,4 kJ/mol. The experimental value of -4,6 kJ/mol for hexyl alcohol (33), is probably too high, the true value is believed to be about -6,4 kJ/mol. For hexanoic acid a value of about -0,9 kJ/mol may be expected. However, as already mentioned, solution enthalpies are rather complex functions and the regularities described above may not be generally valid, especially for compounds with low carbon numbers. Compounds with longer alkyl chains are usually only slightly soluble and experimental investigation of $\Delta H_{\text{soln}}^{\circ}$ becomes very difficult but the development in experimental technique would probably make it possible to test the above assumptions in future.

Solvation enthalpies which can be expressed as:

$$\Delta H_{\text{solv}}^{\circ} = \Delta H_{\text{soln}}^{\circ} - \Delta H_{\text{v}}^{\circ} \quad (6)$$

are less complex than solution enthalpies. Where both enthalpy of solution and enthalpy of vaporisation are known with reasonable accuracy it is thus advantageous to correlate molecular structure and describe solute-solvent interactions in diluted solutions in terms of $\Delta H_{\text{solv}}^{\circ}$ rather than $\Delta H_{\text{soln}}^{\circ}$. There are, unfortunately, only few groups of n-alkyl compounds for which both enthalpies of solution and vaporisation are known. Alkyl amines, n-alkyl alcohols and carboxylic acids form three groups of compounds where both $\Delta H_{\text{v}}^{\circ}$ and $\Delta H_{\text{soln}}^{\circ}$ are known with relatively high accuracy (V). $\Delta H_{\text{solv}}^{\circ}$ of these compounds are plotted against carbon number in Fig. 2. For $\Delta H_{\text{soln}}^{\circ}$ of ethyl amine the above suggested value of -24,4 kJ/mol and for n-hexyl alcohol the value of -6,4 kJ/mol were accepted, with some doubts. The $-CH_2$ -increment has an essentially constant value of $3,4 \pm 0,5$ kJ/mol for both, amines and alcohols. The values of $\Delta H_{\text{v}}^{\circ}$ of carboxylic acids are not very accurate as the experimental vaporisation enthalpies were corrected for non-ideality in vapour phase (IV). The shape of the curve does, however, suggest a similar $-CH_2$ - increment for higher carboxylic acids. It seems apparent that the influence of functional groups on solvation is rather small, as compared to the differences in $\Delta H_{\text{soln}}^{\circ}$. For example, $\Delta H_{\text{soln}}^{\circ}$ of n-butyl- NH_2

and n-butyl-OH differs by 14 kJ/mol but the difference of $\Delta H_{\text{solv}}^{\circ}$ for these compounds is only ca 2,5 kJ/mol. Similarly, the difference in $\Delta H_{\text{soln}}^{\circ}$ for n-propyl-COOH and n-propyl-NH₂ is about 22 kJ/mol, as compared with the difference in $\Delta H_{\text{solv}}^{\circ}$ of about 2,5 kJ/mol.

The shape of the curves $\Delta H_{\text{solv}}^{\circ}$ versus carbon number (Fig. 1) suggests that enthalpies of solvation probably are a linear function of carbon number at $n \geq 3$ and may be expressed by equation:

$$\Delta H_{\text{solv}}^{\circ} = A + n.B \text{ kJ/mol} = A + 3,4.n \text{ kJ/mol} \quad (7)$$

where A is a constant typical for a chosen series of compounds, n is the carbon number and B is the -CH₂- increment (= 3,4 kJ/mol).

The values of the constant A can be derived from the linear parts of the plots on Fig. 2. Thus a value of -45 kJ/mol was derived for amines, -50 kJ/mol for carboxylic acids and -47,5 kJ/mol for alcohols.

It was already mentioned that the function group probably influences the α -methylene groups most and, possibly also, the β -methylene group, as may be deduced from the irregularities in $\Delta H_{\text{soln}}^{\circ}$ and/or in $\Delta H_{\text{solv}}^{\circ}$. It is possible, that the dependence of $\Delta H_{\text{soln}}^{\circ}$ and $\Delta H_{\text{solv}}^{\circ}$ of pure hydrocarbons on the chain length will be of the same order, the -CH₂- increment being about 1-1,5 kJ/mol for $\Delta H_{\text{soln}}^{\circ}$ and about -3,4 kJ/mol for $\Delta H_{\text{solv}}^{\circ}$. The $\Delta H_{\text{V}}^{\circ}$ increment as suggested by Morawetz (37) is about 5 kJ/mol, which is in agreement with the above assumption as follows from the equation:

$$\begin{aligned} \Delta(\Delta H_{\text{V}}^{\circ}) &= \Delta(\Delta H_{\text{soln}}^{\circ}) - \Delta(\Delta H_{\text{solv}}^{\circ}) = (+ 1,5 \text{ kJ/mol}) - \\ &- (- 3,4 \text{ kJ/mol}) = 4,9 \text{ kJ/mol} \end{aligned} \quad (8)$$

Recently, enthalpies of solution and vaporisation were measured for a group of mono and di-glycol ethers (38). The dependence of the derived enthalpies of solvation on the carbon number has been similar as for the compounds considered above. The values fit approximately to Eqn. 7., the constant A has a value of -51,8 kJ/mol and -49,8 kJ/mol respectively.

It is difficult to discuss the general validity of Eqn. 7., since there is a lack of data for other n-alkyl compounds. Especially $\Delta H_{\text{soln}}^{\circ}$ data of hydrocarbons would be of great value because they would reflex pure hydrophobic interactions. The data derived from solubility measurements (39) are probably biased with an appreciable error.

It has been known for a long time that if a molecule containing a hydrophobic part is transferred from liquid state into a water solution, there is a positive change in heat capacity. This phenomenon is now generally understood as evidence for a higher structural order in the water which surrounds the hydrophobic part of the molecule. Disagreement has existed as to the actual values of heat capacity changes, the differences being caused by introduction of large experimental errors on ΔC_{p2}^o and $\bar{C}_{p2}^o$ resp.

Essentially two methods are used to obtain the heat capacity of the solution process. In the first procedure(40, 41) the heat capacities are measured of solutions containing different (low) concentrations of solutes. From the slope of the heat capacity against concentration the value of $\bar{C}_{p2}^o$ can be calculated

$$\bar{C}_{p2}^o = M_2 C_p + (1000 + mM_2) \frac{\partial C_p}{\partial m} \quad (9)$$

where M_2 is the molecular weight of the solute

m is molality

C_p is the heat capacity of the solution

The heat capacity measurements must be made very accurately if the error is to be kept reasonably low.

The second procedure (42) derives ΔC_{p2}^o values from the heats of solution measured at different temperatures. The value of ΔC_{p2}^o is calculated as

$$\Delta C_{p2}^o = \frac{d(\Delta H_{soln}^o)}{dT} = \frac{\Delta(\Delta H_{soln}^o)}{\Delta T} \quad (10)$$

Partial molar heat capacity $\bar{C}_{p2}^o$ can be calculated from ΔC_{p2}^o values using the following formula:

$$\bar{C}_{p2}^o = \Delta C_{p2}^o + C_p^o \quad (11)$$

C_p^o is the heat capacity of pure liquid or solid solute. In Paper V the latter method was used.

The values of ΔC_p^o for a solution process reflect properties not only of the solvated compounds but also intermolecular interactions of the pure solute in the liquid (or solid) state. However, in a series of related liquid compounds, these interactions are supposed to be of the same order of magnitude. As an approximation the pure liquid compounds may often be considered to be, inter alia, in a common reference state. Differences between ΔC_{p2}^o values therefore approximately reflect the extent of interactions

introduced into water by solute molecules.

In Fig. 3 ΔC_{p2}° values of some straight chain amines, carboxylic acids, amides (V) and alcohols (34) are plotted against the carbon number. The values of ΔC_{p2}° of all three groups of compounds from (V) form a nearly straight line. A similar line for alcohols is somewhat higher. The linearity of these values is an indication that in this case the liquid phase can be considered as a valid approximation of a reference state. It should be noted that in analogy to $\Delta H_{\text{soln}}^{\circ}$, ΔC_{p2}° of transfer from a state with no intermolecular interaction would give a better possibility for quantitative explanation of the induced interactions.

The $-\text{CH}_2-$ increment of about 58 J/deg.mol for ΔC_{p2}° seems to be valid for amines, carboxylic acids and amides. (It is interesting to note that the line obtained when ΔC_{p2}° is plotted versus number of alkyl carbons goes through zero on both axis.) The increment for alcohols is somewhat higher i.e. about 62 J/deg.mol and the extrapolated line intersects the ΔC_{p2}° axis at a value of about +14 J/deg.mol. The liquid reference state of the alcohols is probably somewhat different, as compared with the other compounds in this investigation.

In Fig. 4, a similar plot is made for $\bar{C}_{p2}^{\circ}$ values. Partial molar heat capacities reflex only solute - solvent interactions as they are not affected by intermolecular forces among the molecules of the same species. It can be seen that the values fit very well on a straight line, including the $\bar{C}_{p2}^{\circ}$ values for alcohols, and is not dependent on the nature of the hydrophilic group. The derived $-\text{CH}_2-$ increment has a constant value of about 85 J/deg.mol for all the compounds considered here.

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Table 1

Compound	ΔH_f° (g) kJ/mol	ΔH_f° (g, hc) ^{a/} kJ/mol	$\Delta(\Delta H_f^\circ)$ kJ/mol
allyl cyanide	157,7 $\pm$ 1,2	- 0,1 $\pm$ 0,3	157,8 $\pm$ 1,5
cis-1-propenyl cyanide	134,0 $\pm$ 1,0	- 7,0 $\pm$ 0,3	141,0 $\pm$ 1,3
trans-1-propenyl cyanide	140,7 $\pm$ 1,0	- 11,2 $\pm$ 0,3	151,9 $\pm$ 1,3
butyl cyanide	11,1 $\pm$ 1,3	-146,4 $\pm$ 0,3	157,5 $\pm$ 1,6
trans-2-butenyl cyanide	125,6 $\pm$ 1,3	- 31,8 $\pm$ 0,3	157,4 $\pm$ 1,6
cis-1-butenyl cyanide	115,0 $\pm$ 1,3	- 28,1 $\pm$ 0,3	143,1 $\pm$ 1,6
trans-1-butenyl cyanide	119,7 $\pm$ 1,1	- 31,8 $\pm$ 0,3	151,5 $\pm$ 1,4
cyclohexyl cyanide	- 7,2 $\pm$ 0,8	-154,8 $\pm$ 0,3	147,6 $\pm$ 1,1
1-cyclohexen-1-yl-cyanide	101,5 $\pm$ 1,0	- 45,1 $\pm$ 0,3	146,6 $\pm$ 1,3
2-cyclohexen-1-yl-cyanide	109,7 $\pm$ 1,0	- 38,7 $\pm$ 0,3	148,4 $\pm$ 1,3
cyclopentyl cyanide	43,9 $\pm$ 1,0	-106,7 $\pm$ 0,3	150,6 $\pm$ 1,3
1-cyclopenten -1-yl cyanide	141,8 $\pm$ 0,8	- 5,4 $\pm$ 0,3	147,2 $\pm$ 1,1
2-cyclopenten -1-yl-cyanide	156,4 $\pm$ 0,8	+ 8,7 $\pm$ 0,3	147,7 $\pm$ 1,1

a/ ref. 15.

Table 2

Compound	ΔH_V (exp) kJ/mol	ΔH_V° kJ/mol
Formic acid	20,10 $\pm$ 0,04	46,3 $\pm$ 0,5
Acetic acid	23,36 $\pm$ 0,10	51,6 $\pm$ 1,5
Propionic acid	31,14 $\pm$ 0,02	55 $\pm$ 2
Butyric acid	40,45 $\pm$ 0,06	58 $\pm$ 4
Isobutyric acid	35,30 $\pm$ 0,08	53 $\pm$ 4

Table 3

Compound	$\Delta H^\circ_{\text{soln}}$ kJ/mol	$\Delta H^\circ_{\text{solv}}$ kJ/mol	C°_p J/deg.mol	ΔC°_{p2} J/deg.mol	C°_{p2} J/deg.mol
HCOOH (1)	0,678 $\pm$ 0,001	47,0 $\pm$ 0,5	99,0 $\pm$ 0,2	-3,5 $\pm$ 0,5	95,5 $\pm$ 1
MeCOOH (1)	1,176 $\pm$ 0,004	52,8 $\pm$ 1,5	123 $\pm$ 1	42 $\pm$ 2	165 $\pm$ 3
EtCOOH (1)	1,544 $\pm$ 0,004	56,5 $\pm$ 2	151 $\pm$ 1	102 $\pm$ 2	253 $\pm$ 3
PrCOOH (1)	1,460 $\pm$ 0,004	59,5 $\pm$ 4	178 $\pm$ 2	159 $\pm$ 1	337 $\pm$ 3
i-PrCOOH (1)	1,418 $\pm$ 0,004	54,4 $\pm$ 4	173 $\pm$ 1	161 $\pm$ 1	334 $\pm$ 2
BuCOOH (1)	-	-	197 $\pm$ 1	235 $\pm$ 6	432 $\pm$ 7
t-BuCOOH (s)	-2,51 $\pm$ 0,04	-	178 $\pm$ 1	239 $\pm$ 8	417 $\pm$ 9
PrNH ₂ (1)	24,62 $\pm$ 0,02	55,75 $\pm$ 0,10	160 $\pm$ 1	167 $\pm$ 4	327 $\pm$ 5
i-PrNH ₂ (1)	27,45 $\pm$ 0,08	55,05 $\pm$ 0,15	164 $\pm$ 2	178 $\pm$ 16	342 $\pm$ 18
BuNH ₂ (1)	23,33 $\pm$ 0,01	59,04 $\pm$ 0,07	188 $\pm$ 1	234 $\pm$ 3	422 $\pm$ 4
i-BuNH ₂ (1)	23,37 $\pm$ 0,02	57,13 $\pm$ 0,07	194 $\pm$ 1	222 $\pm$ 8	416 $\pm$ 9
t-BuNH ₂ (1)	29,34 $\pm$ 0,03	58,98 $\pm$ 0,07	190 $\pm$ 1	213 $\pm$ 6	403 $\pm$ 7
PeNH ₂ (1)	22,04 $\pm$ 0,02	62,12 $\pm$ 0,07	218 $\pm$ 1	297 $\pm$ 4	515 $\pm$ 5
Hex NH ₂ (1)	20,66 $\pm$ 0,02	65,76 $\pm$ 0,07	252 $\pm$ 2	351 $\pm$ 4	603 $\pm$ 6
MeNHCOEt (1)	14,87 $\pm$ 0,02	-	179 $\pm$ 1	155 $\pm$ 3	334 $\pm$ 4
MeNHCOPr (1)	16,02 $\pm$ 0,02	-	207 $\pm$ 1	227 $\pm$ 4	434 $\pm$ 5
MeNHCO-i-Pr (1)	15,79 $\pm$ 0,02	-	209 $\pm$ 1	222 $\pm$ 5	431 $\pm$ 6
MeNHCOBu (1)	15,03 $\pm$ 0,02	-	229 $\pm$ 1	286 $\pm$ 4	515 $\pm$ 5
MeNHCO-t-Bu (s)	6,26 $\pm$ 0,03	-	183 $\pm$ 1	293 $\pm$ 6	476 $\pm$ 7
EtNHCOMe (1)	15,48 $\pm$ 0,02	-	180 $\pm$ 1	163 $\pm$ 4	343 $\pm$ 5
PrNHCOMe (1)	15,76 $\pm$ 0,02	-	207 $\pm$ 1	230 $\pm$ 4	437 $\pm$ 5
i-PrNHCOMe (1)	17,24 $\pm$ 0,02	-	211 $\pm$ 1	230 $\pm$ 4	441 $\pm$ 5
BuNHCOMe (1)	14,72 $\pm$ 0,03	88,3 $\pm$ 0,8	236 $\pm$ 1	270 $\pm$ 6	506 $\pm$ 5
t-BuNHCOMe (s)	2,54 $\pm$ 0,02	-	190 $\pm$ 1	308 $\pm$ 4	498 $\pm$ 5

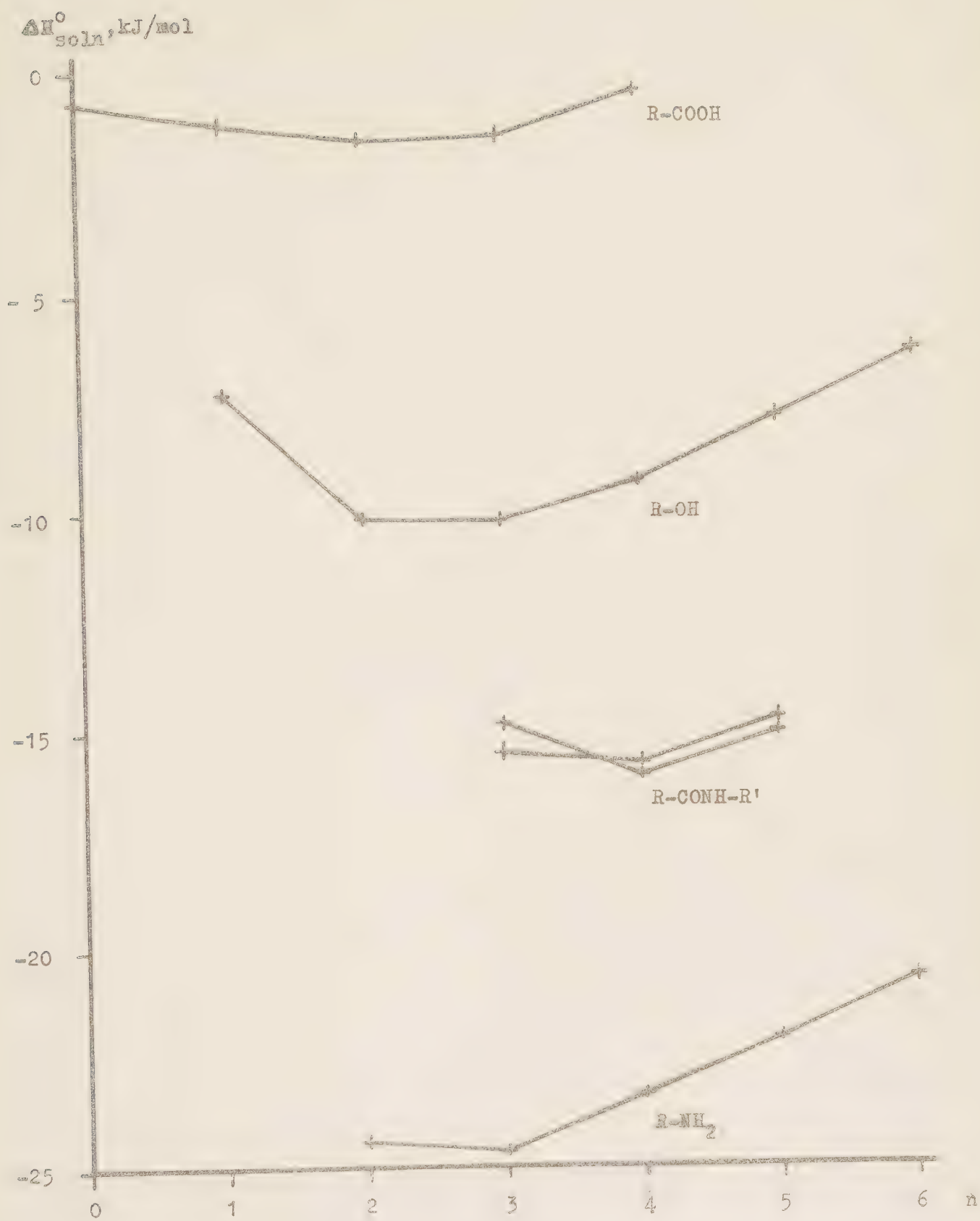


Figure 1.

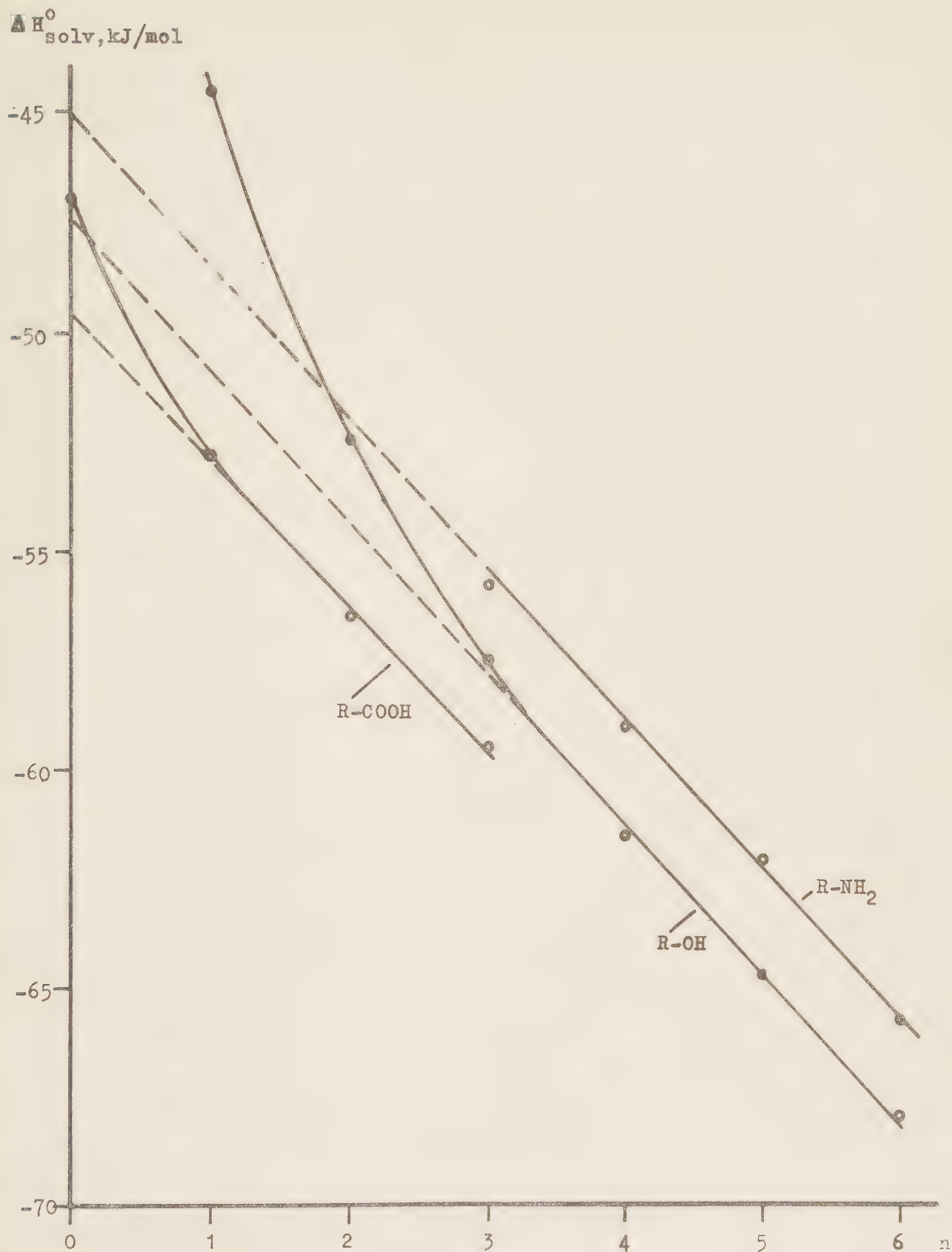


Figure 2.

$\Delta C_{p2}^0, \text{J/deg.mol}$

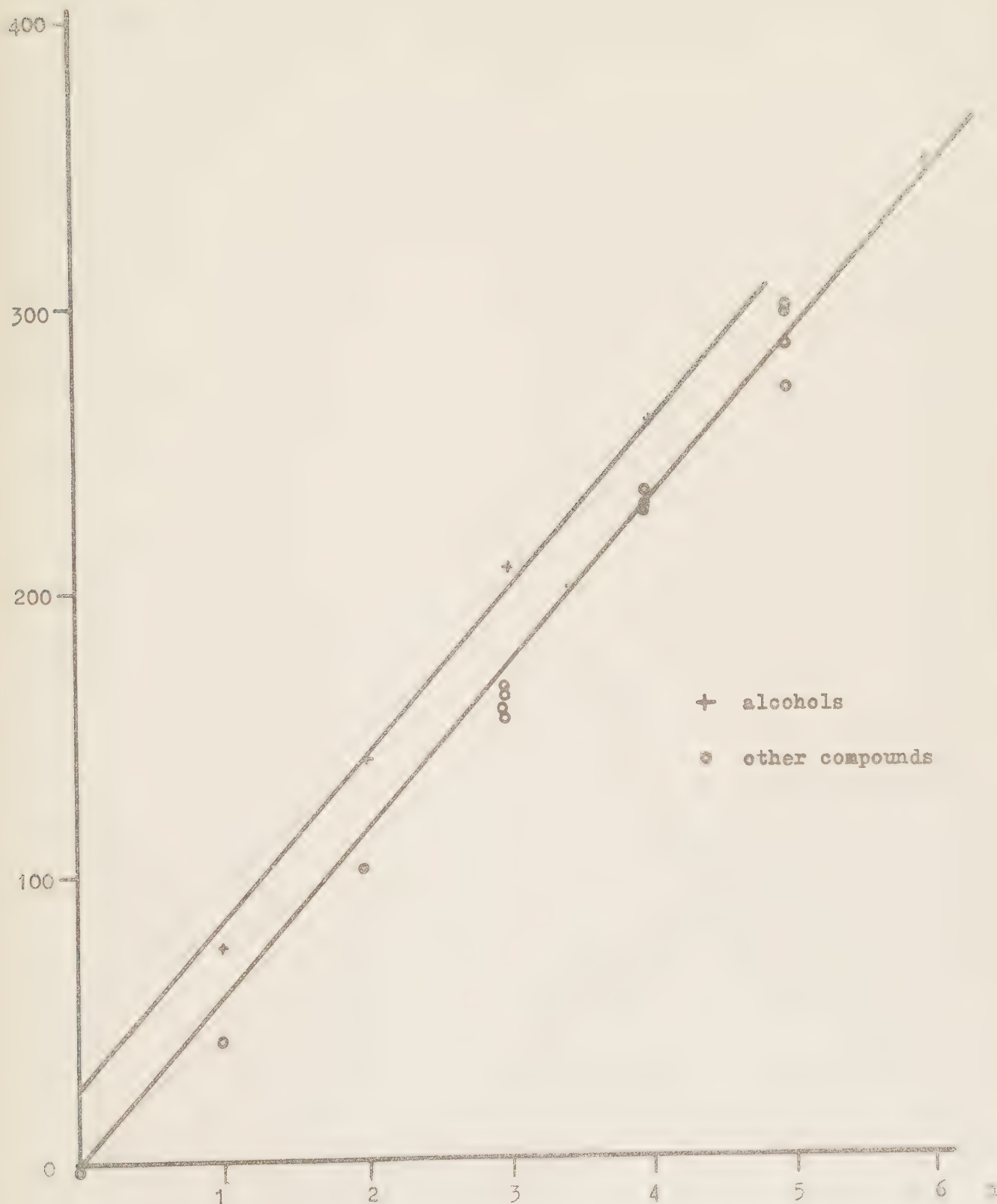


Figure 3.

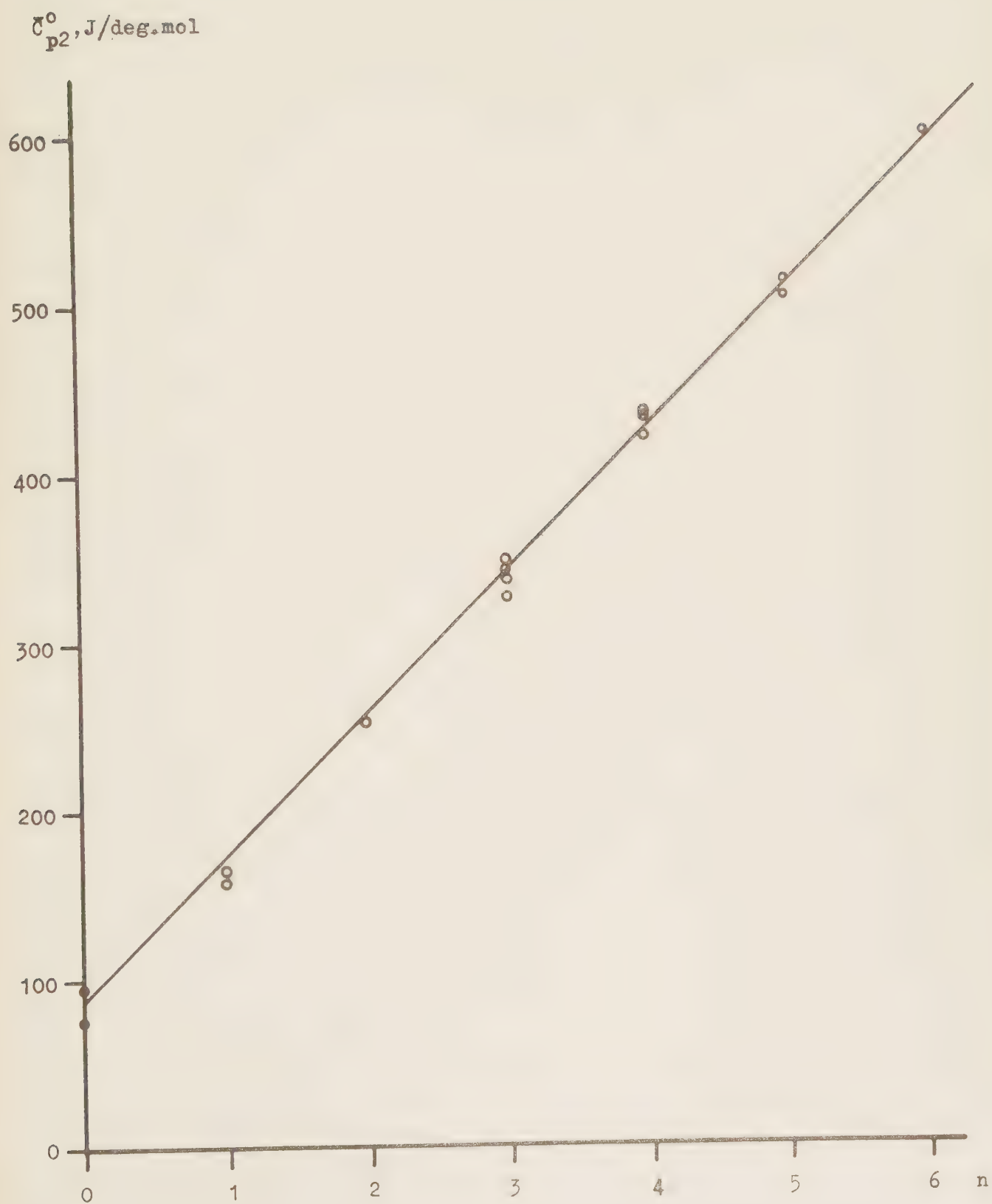


Figure 4.

